

Stabilization in Neutral Bicyclic Sulfoxide Compounds

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ABSTRACT: Density Functional Theory (DFT) calculations at the B3LYP/6-31+G* level have been performed on 5-thiabicyclo[2.1.1]hex-2-ene S-oxide derivatives. The geometrical and electronic properties of the compounds have been analyzed in order to explain the favored stability of the *exo* configuration. Isodesmic reactions at the Gaussian-G2 theory yielded the *exo* conformer as the most stable one. Moreover, the NMR chemical shift parameters (GIAO method) together with the Atoms in Molecules theory reveal an stabilization of the S atom with the double bond for the *exo* configuration, in agreement with the experimental results. © 2000 John Wiley & Sons, Inc. *J Comput Chem* 21: 322–327, 2000

Keywords: *ab initio* calculations; DFT calculations; electronic structure; hypervalent compounds; magnetic properties

Introduction

Non-classical cation chemistry presents noticeable experimental and theoretical aspects.¹ In this context, the electronic structure of the 2-norbornyl cation has raised the strongest controversies in physical organic chemistry,^{2,3} and evidence of extra stabilization for this cation has resulted from extensive research,⁴ generally yielding a good agreement between experimental (X-ray data)^{5,6} and theoretical results,^{7,8} including the comparison of ¹³C chemical shifts.⁹ On the other hand, the special anchimeric acceleration, observed

on 7-norbornadienyl-chloride that solvolyzed 10¹⁴ times faster than 7-norbornyl-chloride and even 10³ times faster than 7-norbornenyl-chloride, has been explained by the exceptional stability of the 7-norbornadienyl cation.^{10,11} Schleyer et al.¹² performed a detailed theoretical study of 7-norbornadienyl and 7-norbornenyl cations, estimating –20.3 and –15.0 kcal/mol energy stabilization by homoaromatic interactions for both cations, respectively. A similar study was also conducted on 7-boranorbornene and 7-boranorbornadiene by Schleyer et al.¹³

As 7-norbornenyl cations, the bicyclo[2.1.1]hex-2-en-5-ylum cations have homoaromatic 3c–2e stabilization.¹⁴ The latter cations are structurally related to the titled compounds considered in

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the present work. The X-ray structure of bicyclo [2.1.1]hex-2-en-5-yl cations have recently been reported,¹⁵ and the theoretical (B3LYP/6-31G*) geometries are in good agreement with the experiment.⁷

The stabilization in 7-norbornenyl and bicyclo [2.1.1]hex-2-en-5-yl cations has been explained as an homoaromatic 3c-2e interaction. However, the stabilization in 7-norbornadienyl and related cations need a more general theoretical description as a (0,2,2) longicyclic interaction.¹⁶

In addition, a search of the CSDS database¹⁷ for a sulfoxide group with the same environment as in 1 or 2 with respect to the double bond yielded only structures with *exo* oxygen configuration.^{18–20}

The quantum-mechanical theory of atoms in molecules (AIM), proposed by Bader, makes it possible to define atomic and bond properties without resorting to the unjustified identification of basis

functions as atomic orbitals. On the other hand, theoretical methods of substantial quality can be used to calculate NMR data using the GIAO method, yielding data comparable with the experiment.

The goal of the present work is to study the stabilization in neutral molecules, performing accurate quantum-chemistry calculations on 5-thiabicyclo[2.1.1]hex-2-ene S-oxide derivatives. Given the special bond nature of the sulfoxide groups, and in view of our recent results on related compounds²¹ or sulfoxide derivatives,²² a net and large amount of positive charge is produced on sulfur (see Fig. 1).

Computational Methods

Density functional theory (B3LYP/6-31+G*) and Gaussian-G2²³ calculations were performed with

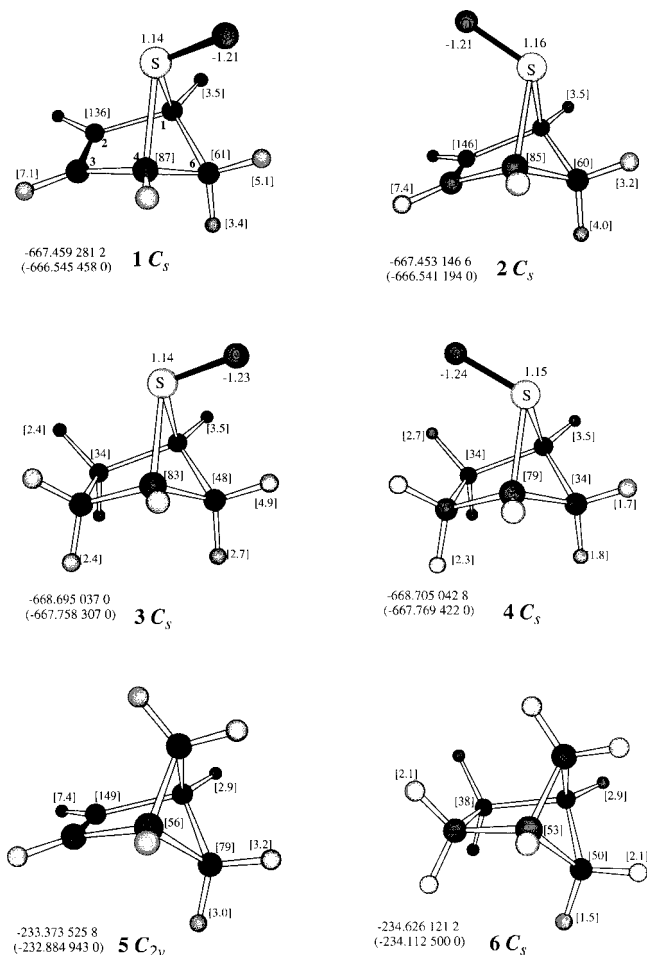


FIGURE 1. Theoretical structures 1–6, including symmetry, atom numbering, total energies, G-2 energies (in parentheses), together with the atomic charges for the S and O atoms and ¹³C, ¹H-NMR chemical shifts [in brackets] calculated at the B3LYP/6-31+G* level.

TABLE I.
Geometrical Parameters^a (Å, Degrees) Calculated at the B3LYP/6-31+G* Theoretical Level, for Structures 1–6.

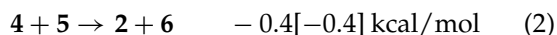
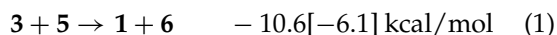
	1	2	3	4	5	6
C ₂ —C ₃	1.352	1.344	1.568	1.560	1.336	1.568
C ₁ —X ₅ ^b	1.997	1.962	1.918	1.905	1.568	1.556
S ₅ —O ₇	1.506	1.502	1.514	1.511	—	—
H ₆ ···O ₇	2.660	—	2.532	—	—	—
S ₅ ···C ₂	2.584	2.711	2.670	2.684	—	—
∠C ₂ C ₁ C ₄ X ₅ ^b	−105.9	−115.9	−111.1	−113.2	−116.4	−114.9

^a See numbering in Figure 1.^b X = C or S.

the Gaussian 98 package of programs.²⁴ All the structures were fully optimized with constrained C_{2v} or C_s symmetries, and tested with frequency calculations (no imaginary frequencies). The AIM analysis has been made with the AIMPAC²⁵ series of programs, using the DFT density as input, as described in the AIM theory.^{26, 27} The ¹³C and ¹H-NMR chemical shift were calculated with the GIAO method²⁸ using their corresponding TMS shielding as a reference.

Results and Discussion

Geometry optimization, at the B3LYP/6-31+G* level, has been performed on the structures presented in Figure 1. At this level, structure **1** is more stable than **2** by 3.9 kcal/mol, despite the steric interactions between the oxygen and the β hydrogen at C₆. The energy difference, in the saturated compounds, favored **4** vs. **3** by 6.3 kcal/mol, in which there is no possible interaction between the oxygen atom and the abovementioned hydrogen. The stabilization has been evaluated by means of isodesmic reactions:



the above eqs. (1) and (2) indicated a net stabilization for one of the S—O group configurations (*exo* with respect to the double bond, structure **1**). The *endo* configuration (structure **2**) showed a low stabilization energy. These results have also been tested with accurate G-2 isodesmic calculations, and the results are depicted in brackets in eqs. (1) and (2).

The stabilization of structure **1** deserved further study to characterize these electronic interactions. The geometrical parameters of **1** and **2** are depicted in Table I, together with the saturated structures **3**

and **4**, and hydrocarbons **5** and **6**. For this interaction, a clear participation of the olefinic electrons is evident from the geometrical parameters.

Thus, the C₂—C₃ bond lengths for both structures **1** and **2** were greater than for the olefinic hydrocarbon **5**, with structure **1**, showing larger deviations (ca. 0.016 Å). In addition, the S···C₂ distance shortens for structure **1** (2.548 Å), but remained similar for **2** and for the saturated compounds **3** and **4** (ca. 2.7 Å). Moreover, the ∠C₂C₁C₄S dihedral revealed a similar trend, with smaller values for structure **1**. The C₁—S distance lengthened by more than 0.03 Å from **1** to **2** (*exo* vs. *endo* configuration, respectively), in addition, this distance also increased for **2** in comparison with the saturated structures **3** and **4**.

All the geometrical features discussed above demonstrated that the sulfur bridge approaches the double bond due to the stabilization in **1** (*exo*), as found experimentally in bicyclo[2.1.1]hex-2-ene 5-yl cation derivatives.¹⁵

Theoretical ¹³C and ¹H-NMR chemical-shift calculations have become extremely useful tools in structural chemistry, as exemplified by Schleyer et al. in the study of the 7-norbornadienyl cation,¹² and its 7-borane derivative.¹³ Theoretical GIAO ¹³C and ¹H calculations were performed and the results displayed in Figure 1. The participation of the C₂—C₃ double bond in the stabilization of **1** is clearly shown by comparing its ¹³C chemical shifts with structure **2** (135.7 vs. 146.4 ppm, respectively). This upfield shift is compatible with a larger electron delocalization, and has also been demonstrated experimentally for 7-norbornenyl and 7-norbornadienyl cations.^{29, 30} However, Schleyer et al.,¹² from calculations on 7-norbornadienyl cation, have reported opposite behavior. These contradictory results appear to be attributable to an error in the ¹³C assignments.¹² Moreover, carefully theoretical

TABLE II.

Charge Density, $\rho(r)$, Laplacian of the Charge Density, $\nabla^2\rho(r)$, Ellipticity, ε , and Local Energy Density, $E_d(r)$, for the Bond Critical Points (BCPs) of Structures 1–6, at the B3LYP/6-31+G* Theoretical Level.

	$\rho(r)$ (e/a_0^3)	$\nabla^2\rho(r)$ (e/a_0^5)	ε	$E_d(r)$ (hartree/ a_0^3)		$\rho(r)$ (e/a_0^3)	$\nabla^2\rho(r)$ (e/a_0^5)	ε	$E_d(r)$ (hartree/ a_0^3)
1					3				
S—O	0.256	0.772	0.005	−0.288	S—O	0.255	0.601	0.005	−0.294
S—C ₁	0.134	−0.109	0.070	−0.067	S—C ₁	0.158	−0.201	0.051	−0.093
C ₁ —C ₂	0.262	−0.614	0.091	−0.223	C ₁ —C ₂	0.245	−0.544	0.024	−0.195
C ₂ —C ₃	0.334	−0.932	0.320	−0.360	C ₂ —C ₃	0.228	−0.482	0.007	−0.172
C ₁ —H ₁	0.277	−0.973	0.002	−0.276	C ₁ —H ₁	0.275	−0.956	0.002	−0.273
2					4				
S—O	0.258	0.772	0.008	−0.292	S—O	0.255	0.656	0.007	−0.292
S—C ₁	0.144	−0.143	0.032	−0.077	S—C ₁	0.160	−0.206	0.055	−0.096
C ₁ —C ₂	0.254	−0.582	0.074	−0.209	C ₁ —C ₂	0.245	−0.543	0.028	−0.190
C ₂ —C ₃	0.341	−0.967	0.344	−0.375	C ₂ —C ₃	0.231	−0.494	0.004	−0.170
C ₁ —H ₁	0.277	−0.967	0.002	−0.275	C ₁ —H ₁	0.276	−0.955	0.002	−0.273
5					6				
C ₅ —C ₁	0.228	−0.469	0.007	−0.174	C ₅ —C ₁	0.233	−0.492	0.004	−0.181
C ₁ —C ₂	0.243	−0.541	0.061	−0.194	C ₁ —C ₂	0.241	−0.532	0.019	−0.190
C ₂ —C ₃	0.342	−0.962	0.351	−0.378	C ₂ —C ₃	0.229	−0.483	0.015	−0.173
C ₁ —H ₁	0.274	−0.929	0.002	−0.268	C ₁ —H ₁	0.272	−0.917	0.002	−0.265

^{13}C calculations at the B3LYP/6-31+G* level for the C_s 7-norbornadienyl cation yielded 113.8 and 123.3 ppm for the C₂ and C₅ carbon atoms, respectively. The aforementioned ^{13}C upfield shift is ascribed to the interaction of the S atom and the double bond, because for **3** and **4**, with the same spatial arrangements, there is only a very slight shift on C₂ (34.2 and 33.6 ppm for **3** and **4**, respectively). In addition, this upfield shift is also found in ^1H -NMR data (7.1 and 7.4 ppm for H-2 on structures **1** and **2**, respectively). The stabilization on this structure has also been analyzed by means of the AIM theory.^{26, 27}

Table II gives the numerical values at the bond critical points (BCPs) for structures 1–6. The main differences appear at the C₂—C₃ BCPs for **1** and **2**, showing smaller $\rho(r)$, $-\nabla^2\rho(r)$, ε , and $E_d(r)$ values for **1** than for structure **2** (compatible with a weaker double bond). The lengthening in the C₁—S bond agreed with the corresponding BCPs properties, the $\rho(r)$ values increased as the bond length decreased; however, the ε value for **1** was the largest one. All the above indicated a participation of the C₁—S bond in the proposed stabilization interaction, possibly by participation of the C₁—S and C₄—S σ^* orbitals.³¹ The atomic charges at the sulfur atom (Fig. 1) showed a value independent of the *exo/endo*

configuration and of the existence of a double bond. For the titled compounds, the observed stabilization in the *exo* configuration cannot be defined as the homoaromatic stabilization (3c–2e interaction) proposed for the 7-norbornenyl cations.

The quantum mechanical pair density in conjunction with the quantum definition of an atom in a molecule, provides a precise determination of the extent to which electrons are localized in a given atom and delocalized over any pair of atoms.³² The electron pairing is a consequence of the Pauli exclusion principle, and the extent of spatial localization of the pairing is determined by the corresponding property of the Fermi hole density. These ideas are made quantitative through the appropriate integration of the pair density to determine the total Fermi correlation contained within a single atomic basin, the quantity $F(A,A)$, or $F(A,B)$, the correlation shared between two basins. The quantity $F(A,B)$ is, thus, a measure of the extent to which electrons of either spin referenced to atom A are delocalized onto atom B with a corresponding definition of $F(B,A)$. Thus, $F(B,A) = F(A,B)$ and their sum, $F(A,B) + F(B,A) = \delta(A,B)$ termed the *delocalization index*, is a measure of the total Fermi correlation shared between the atoms. This *delocalization index*

TABLE III.
Delocalization Indexes between Different Atoms
Calculated at the B3LYP/6-31+G* Theoretical Level,
for Structures 1–4.

	1	2	3	4
$\delta(\text{C}_2, \text{C}_3)$	1.672	1.740	0.958	0.959
$\delta(\text{S}, \text{C}_1)$	0.785	0.814	0.861	0.863
$\delta(\text{S}, \text{O})$	1.414	1.418	1.386	1.378
$\delta(\text{S}, \text{C}_2)$	0.140	0.092	0.060	0.056
$\delta(\text{C}_1, \text{C}_2)$	1.053	1.020	0.974	0.982
$\delta(\text{C}_1, \text{C}_3)$	0.079	0.077	0.053	0.051

is formulated taking into account that:

$$F(A, B) = F(B, A) = - \sum_i \sum_j S_{ij}(A) S_{ij}(B) \quad (3)$$

where $S_{ij}(A)$ is the corresponding atomic overlap matrix given by with the PROAIM program.²⁵ The calculated $\delta(A, B)$ are listed in Table III for structures 1–4. The corresponding $\delta(\text{C}_2, \text{C}_3)$ values for 1 were smaller than for 2, yielding larger $\delta(\text{S}, \text{C}_2)$ values for 1 than for 2 (0.14 vs. 0.09). In addition, the same index for 3 and 4 was ca. 0.06, indicating independence with the SO orientation. Moreover, the $\delta(\text{C}_2, \text{C}_3)$ values for 3 and 4 remained unchanged. The $\delta(\text{C}_1, \text{C}_2)$ is also higher for the *exo* configuration in the unsaturated compound 1, and this index for 1 and 2 is larger than those for the saturated structures (3 and 4). Moreover, the $\text{C}_1\text{—C}_2$ bond length for 1 is shorter than for 2. There is also a small delocalization index, $\delta(\text{C}_1, \text{C}_3)$, higher for 1 and 2 than for 3 and 4.

All the above data disagreed with the aforementioned homoaromatic stabilization of the residual positive charge on the S atom by the double bond (the sulfur charge remained unchanged for 1–4). However, there is a net electronic delocalization in 1 between the S, C_2 , and C_3 atoms, together with a lengthening in the S—C_1 and S—C_4 bonds, and a shortening in the $\text{C}_1\text{—C}_2$ and $\text{C}_3\text{—C}_4$ bonds. This is compatible with the participation in the interaction of the S atom lone pair for the *exo* configuration (the *endo* having the lone pair away from the double bond). Such pericyclic [2+2] interaction is clearly unstabilized; however, the participation of the σ^* bonds (S—C_1 and S—C_4) yielded stabilizing (0,2,0,2) longicyclic interaction.¹⁶

Test calculations have also been performed on the $\text{H}_2\text{C=CH}_2 \cdots \text{H}_2\text{S=O}$ complex, in which there are no possible S—C σ^* orbitals, and the results indicated the existence of only a van der Waals type com-

plex with large $\text{S} \cdots \text{C}$ distance (3.579 Å) and low interaction energy (2.0 kcal/mol at the B3LYP/6-31G* level). Moreover, preliminary computations on 5-phosphabicyclo[2.1.1]hex-2-ene yielded an stabilization (2.2 kcal/mol) of the structure with an *exo* P—H bond and an *endo* lone pair with respect to the *endo* P—H bond structure.

Conclusions

A net stabilization on neutral bicyclo sulfoxide derivatives has been theoretically demonstrated here when a $\text{C}_2\text{—C}_3$, double bond is present. In the titled compounds, further stabilization is corroborated when the S—O bond adopted an *exo* configuration with respect to the double bond. This stabilization agreed with the theoretical evidence [geometrical, energetic (Gaussian G-2 method), and ^{13}C , ^1H -NMR calculations, together with electron delocalization data]. The stabilization responsible for the preferred *exo* configuration (structure 1) has been proposed as a (0,2,0,2) longicyclic interaction with participation of the sulfur electron pair.

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